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**STRUCTURE AND PROPERTIES OF TERNARY ALLOYS WITH THORIUM**

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The report deals with the experimental data obtained by the authors on the structure of ternary alloys containing thorium in the solid state in the ternary systems: thorium – zirconium-titanium; thorium – zirconium – cerium, thorium – zirconium – niobium and thorium – zirconium-niobium and thorium – zirconium-molybdenum. Consideration is given to the study of metastable phases, conditions of their formation and their relation to the properties of alloys. The results of the investigation are derived for the most part from the data of X-ray and microstructure analyses as well as the hardness of specimens quenched after holding for a long period of time.

Alongside with the earlier published data on equilibrium diagrams of the ternary systems: thorium – zirconium – uranium (1) and thorium zirconium – niobium (2), on the structure of thorium – zirconium – carbon alloys representing thorium – zirconium carbide by section (2), thorium – beryllium – uranium alloys representing  $\text{Th Be}_{13}$  –  $\text{U Be}_{13}$  by section (1) thorium – silicon – uranium alloys representing  $\text{Th Si}_2$  –  $\text{USi}_2$  by section (2) as well as the results of studying some mechanical and corrosion resisting properties of these alloys (2), this investigation reveals the character of thorium interaction in ternary alloys with a number of most interesting elements as well as enables to point out some peculiarities of their properties. In choosing the systems the authors took into consideration the possibility of forming wide regions of solid solutions with thorium, the possibility of improving its corrosion resisting properties, as well as relatively small value of thermal neutron capture by alloying elements.

**1. THE THORIUM-ZIRCONIUM-TITANIUM SYSTEM**

At high temperatures including 100°C thorium-zirconium-titanium system is characterized by the presence of a wide region of solid solutions based on the body-centered cubic lattice of  $\beta\text{Th-Zr-Ti}$ . This results from the existence of continuous ranges of solid solutions between  $\beta$  – modifications of metals in limiting thorium – zirconium and zirconium – titanium binary systems; as is known thorium and titanium form between each other a simple eutectic diagram with highly limited regions of solid solutions. Henceforth  $\beta$  solid solution of thorium – zirconium – titanium system will be designated as  $\beta_{\text{Zr}}$  if it contains more than 50 at. % zirconium and as  $\beta_{\text{Th}}$  if it contains less than 50 at. % zirconium and by composition approaches thorium – zirconium binary system and as  $\beta_{\text{Ti}}$  if it contains less than 50 at. % of zirconium and adjoins the side of zirconium – titanium.

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The peculiarity of the system consists also in the presence of a decomposition region into two solid solutions  $\beta_{\text{Th-Zr}} + \beta_{\text{Zr}}$  with similar crystal lattice but with different content of components. At high temperatures this decomposition region limits the region of  $\beta$  solid solution of Th-Zr-Ti as it is indicated in Fig.1, where isothermal sections of the equilibrium diagram of thorium-zirconium - titanium system at 930, 900, 800 and 600°C are given; the boundaries of phase regions at 1000°C are shown by dotted lines on the projection of the equilibrium diagram of the system (fig. 2). When the temperature is lowered to 930°C (fig. 1a) the region of  $\beta$  solid solution of Th-Zr-Ti diminishes due to the joining of the decomposition region  $\beta_{\text{Th-Zr}} + \beta_{\text{Zr}}$  in the ternary system to the decomposition region  $\beta_{\text{Th}} + \beta_{\text{Zr}}$  in the thorium - zirconium binary system. At 900°C (fig. 1b) a wide two-phase region  $\alpha_{\text{Th}} + \beta_{\text{Zr}} + \text{Ti}$  goes from the thorium - zirconium binary system to the thorium - titanium binary system. At this temperature in the ternary system the decomposition region  $\beta_{\text{Th-Zr}} + \beta_{\text{Zr}}$  no longer exists indicating to the fact that the decomposition region ( $\beta_{\text{Th}} + \beta_{\text{Zr}}$ ) from the thorium - zirconium binary system into the thorium - zirconium - titanium ternary system does not spread to low temperature region.

At 800°C (fig. 1c) the region of  $\beta_{\text{Zr}}$  solid solution appreciably narrows and at 600°C (fig. 1d) the majority of the alloys investigated are in two-phase regions:  $\alpha_{\text{Th}} + \alpha_{\text{Zr}}$ ;  $\alpha_{\text{Th}} + \beta_{\text{Zr-Ti}}$  and  $\alpha_{\text{Th}} + \alpha_{\text{Ti}}$ . The boundaries of three-phase regions on the isothermal sections of the equilibrium diagram of the thorium - zirconium - titanium system at 800 and 600°C are shown by dotted lines since in this concentration regions only some alloys were studied. At 500°C all alloys investigated are in two phase state  $\alpha_{\text{Th}} + \alpha_{\text{Zr-Ti}}$ ; here there are only highly limited regions of hard solutions  $\alpha_{\text{Th}}$  and  $\alpha_{\text{Zr-Ti}}$  which are closely approaching the binary systems thorium - zirconium and zirconium - titanium.

Crystalline structure of the alloys quenched at various temperatures within 1000-600°C is shown on isothermal sections of the equilibrium diagram (fig.1). In the alloys of  $\beta_{\text{Th-Zr-Ti}}$  solid solution, rich in zirconium and titanium it is characterized by hexagonal lattice  $\alpha'_{\text{Zr}}$  or  $\alpha'_{\text{Ti}}$  representing solid solutions based on hexagonal lattice of  $\alpha_{\text{Zr}}$  or  $\alpha_{\text{Ti}}$  respectively supersaturated by two other components. The presence of hexagonal lattice in these alloys is caused by  $\beta \rightarrow \alpha'$  transformation taking place during their quenching. In the alloys of  $\beta_{\text{Zr}}$  solid solution (15 at. % titanium + 70 at.% zirconium), (25 at. % titanium + 65 at. % zirconium) and (40 at.% titanium + 44 at.% zirconium) which are close by their composition to the maximum saturation after quenching at 1000° - 900°C a body centered cubic lattice of  $\beta_{\text{Zr}}$  solid solution is observed. In the alloys quenched from the region of  $\beta_{\text{Th}}$ , as well as  $\beta_{\text{Zr}}$  solid solutions containing 50 and 60 at% zirconium and less than 3 at.% titanium a face centered cubic lattice  $\alpha_{\text{Th}}$  is observed due to decomposition of the concentration, which is also observed in the thorium - zirconium binary alloys of the same concentration (1).

In accordance with crystal lattices of the alloys quenched from the region of  $\beta_{\text{Th-Zr-Ti}}$  solid solution, in two-phase regions of  $\beta_{\text{Th-Zr}} + \beta_{\text{Zr}}$  and  $\alpha_{\text{Th}} + \beta_{\text{Zr-Ti}}$  a face centered cubic  $\alpha_{\text{Th}}$  and body centered cubic  $\beta_{\text{Zr}}$  lattices are respectively observed as well as  $\alpha_{\text{Th}}$ ,  $\beta_{\text{Zr}}$  and hexagonal lattice  $\alpha_{\text{Ti}}$ . The alloys of these regions which are rich in thorium have the lattice  $\alpha_{\text{Th}}$ ; in the region  $\alpha_{\text{Th-Zr}} + \beta_{\text{Zr}}$  the alloy with 60 at.% zirconium in the section cutting the zirconium

corner of the system at a ratio of Th:Ti = 1:1 has a body centered cubic lattice  $\beta_{Zr}$ ; in the region  $\alpha_{Th} + \beta_{Zr-Ti}$  the alloys located in the section cutting the zirconium corner of the system at a ratio of Th:Ti = 1:1 and containing up to 55 at.% titanium have two lattices:  $\alpha_{Th}$  and  $\alpha_{Ti}$ . At increasing titanium content in the alloys of this region only  $\alpha_{Ti}$  lattice is observed.

At quenching the alloys from the region of  $\beta_{Zr}$  - solid solution at 800°C the authors failed to observe body centered cubic lattice in any of the alloys investigated. In conformity with this in the alloys quenched from two-phase regions  $\alpha_{Th} + \beta_{Zr-Ti}$  and  $\alpha_{Th} + \alpha_{Ti}$  at 800°C  $\alpha_{Th}$  lattice is observed as well, in the alloys located in the section, cutting the zirconium corner of the system at a ratio of Th:Ti = 1:1  $\alpha_{Ti}$  is observed; as well as in the alloys with 5-25 at.% thorium and 50 and more at.% zirconium; in the alloys located from the section, cutting the zirconium corner of the system at a ratio of Th:Ti = 1:1 closer to the side of increasing of thorium content  $\alpha_{Th}$  is observed and in the alloys adjoining by their composition the boundaries of  $\beta_{Ti}/\alpha_{Th} + \beta_{Zr-Ti}$  and  $\alpha_{Ti}/\alpha_{Th} + \alpha_{Ti}$   $\alpha_{Ti}$  is observed. Investigation of crystal lattices of the alloys, quenched at 600 and 500°C shows nothing new in comparison with the data, obtained for the alloys, quenched at 800°C.

According to the data, obtained in studying the structure of the quenched thorium - zirconium titanium alloys a projection of the equilibrium diagram has been plotted and a reaction scheme was made (fig.2). Lines on the projection of the diagram (fig. 2a) describe transformation processes in the solid state at the temperature from 1000 to 500°. At 1000°C as a result of the presence of a lamination region  $\beta_{Th-Zr} + \beta_{Zr}$  in the ternary system there exists an equilibrium  $\alpha_{Th} + \beta_{Th} + \beta_{Zr}$ . When the temperature is lowered this equilibrium reaches the thorium - zirconium binary system (curves  $\beta_{Zr} - \beta^1_{Zr}$ ,  $\beta_{Th} - \beta^1_{Th}$  and  $\alpha_{Th} - \alpha^1_{Th}$ ) and comes to an end at 920°C  $\beta^1_{Th} \rightleftharpoons \alpha^1_{Th} + \beta^1_{Zr}$  by reaction. As a result of superposing of three-phase equilibrium  $\beta^2_{Ti} \rightleftharpoons \alpha^2_{Th} + \alpha^2_{Ti}$  at 882°C, coming from the thorium - titanium binary system and three-phase equilibrium  $\beta^3_{Zr} \rightleftharpoons \alpha^3_{Th} + \alpha^3_{Zr}$ , coming from the thorium - zirconium binary system (curves  $\beta^2_{Ti} - \beta^3_{Zr}$  and  $\alpha^2_{Ti} - \alpha^3_{Zr}$ ) in the ternary system three-phase equilibrium  $\beta^{3-2}_{Zr-Ti} \rightleftharpoons \alpha^{3-2}_{Zr-Ti} + \alpha^{3-2}_{Th}$  is set at ~520°C. This equilibrium in the ternary system is propagated to the regions of more lower temperatures as well, up to room temperature.

## 2. THE THORIUM - ZIRCONIUM - CERIUM SYSTEM

In the thorium - zirconium - cerium system there is no wide range of ternary solid solutions based on a body centered cubic lattice of  $\beta$  - zirconium. This region is limited by too low solubility of cerium in zirconium in the solid state. Below 920°C the decomposition region of  $\beta$  solid solution into two solid solutions of  $\beta_{Th} + \beta_{Zr}$  in the thorium - zirconium binary system does not spread over the ternary system thorium - zirconium - cerium; at 930°C the alloys of these region contain less than 1 at.% cerium. The region of  $\alpha_{Th-Zr-Ce}$  solid solution in the ternary system by its composition adjoins the thorium - cerium binary system; at 930°C the solubility curve approaches an additive strait line and goes from 13.5 at. % zirconium in the thorium - zirconium binary system to 7 at.% zirconium in the section, cutting the zirconium corner of the system at a ratio of Th:Ce = 1:1. When the temperature is lowered down to

600°C the region of  $\alpha_{\text{Th-Zr-Ce}}$  solid solution narrows noticeably; the zirconium content in the alloys of this region decreases from 6 at.% in the thorium – zirconium binary system to 1 at.% in the section cutting the zirconium corner of the system at a ratio of  $\text{Th} : \text{Ce} = 1 : 1$ .

930°C, 900°C, 680°C and 600°C isothermic sections of the equilibrium diagram of the thorium – zirconium – cerium system are given in Fig. 3. At 930° and 900°C the isothermic sections characterize the structure of the ternary alloys, which are rich in thorium.

By preliminary experiments on quenching thorium – zirconium – cerium alloys at 1000°C it was found that the region of ternary solid solution based on  $\beta_{\text{Zr}}$  in the section cutting the zirconium corner of the system at a ratio of  $\text{Th} : \text{Ce} = 1 : 1$  does not surpass 1 at.% ( $\text{Th} + \text{Ce}$ ). The region of ternary  $\beta$  solid solution at this temperature approaches closely the binary system: thorium – zirconium.

At 930°C (fig. 3a) there exists a very narrow region of  $\beta$  solid solution based on the body-centred cubic lattice of  $\beta$  zirconium, which closely approaches by its composition the thorium – zirconium binary system, containing more than 66 at.% zirconium and less than 0.5 at.% cerium. The region of the ternary  $\alpha_{\text{Th-Zr-Ce}}$  solid solution spreads from 13.5 at.% zirconium in the binary system thorium-zirconium to 7 at.% zirconium in the section cutting the zirconium corner of the system at a ratio of  $\text{Th} : \text{Ce} = 1 : 1$ . The curve of mutual solubility of zirconium and thorium at this temperature shows a relationship close to an additive one. Also at this temperature a narrow region of decomposition into two solid solutions  $\beta_{\text{Th}} + \beta_{\text{Zr}}$  extends from the thorium – zirconium binary system to the ternary system at concentration interval of 43 to 68 at.% zirconium; the alloys of this region contain less than 1 at.% cerium. Here a very narrow region of three-phase state of alloys  $\alpha_{\text{Th}} + \beta_{\text{Th}} + \beta_{\text{Zr}}$  is outlined which is limited by three two-phase regions  $\beta_{\text{Th}} + \beta_{\text{Zr}}$ ,  $\alpha_{\text{Th}} + \beta_{\text{Th}}$  and wide region  $\alpha_{\text{Th-Zr-Ce}} + \beta_{\text{Zr}}$ . At 930°C high cerium alloys as well as those approaching by composition to the zirconium – cerium binary system contain the liquid phase.

All the alloys, shown in Fig. 3a which are quenched at 930°C have a face-centred cubic structure of solid solution  $\alpha_{\text{Th-Zr-Ce}}$ . In alloys of a section with constant 55 at.% thorium content which are in two-phase region  $\beta_{\text{Th}} + \beta_{\text{Zr}}$ , the presence of  $\alpha_{\text{Th}}$  lattice is connected with the decomposition of the  $\beta_{\text{Th}}$  phase in this region of compositions (1).

At the temperature of 900°C two-phase region  $\alpha_{\text{Th-Zr-Ce}} + \beta_{\text{Zr}}$  (fig. 3b) reaches the thorium-zirconium binary system, indicating that the reaction of decomposition of the  $\beta_{\text{Zr}}$  solid solution having a body-centred cubic lattice into two solid solutions with the same lattice, but with different content of components  $\beta_{\text{Th}} + \beta_{\text{Zr}}$ , does not spread over the ternary system thorium – zirconium – cerium when the temperature is lowered to 900°C. As is seen in fig. 3b, at 900°C the region of the  $\beta_{\text{Zr}}$  solid solution is somewhat narrowed as compared with this region at 930°C (the minimum zirconium content in it increases up to 72 at.%). The region of solid solution  $\alpha_{\text{Th-Zr-Ce}}$  is limited by a parabolic line which passes from 13 at. % zirconium in the thorium – zirconium binary system to 6 at.% zirconium in the section cutting the zirconium corner at a ratio of  $\text{Th} : \text{Ce} = 1 : 1$ . Crystal lattice of the studied alloys quenched at 900°C is the same as that of alloys quenched at 930°C, i.e. a face-centered cubic one. At 900°C as at the temperature of 930°C, there exists a region of alloys rich in cerium and zirconium and containing the liquid phase.

At 680°C alloys of the thorium-zirconium-cerium system are in the solid state at the whole interval of the concentration. As is shown in fig. 3c, two-phase region  $\alpha_{\text{Th-Zr-Ce}} + \beta_{\text{Zr}}$  to which a narrow region of solid solution  $\alpha_{\text{Th-Zr-Ce}}$  approaches occupies a wide region of concentrations. Here a region of three-phase state of alloys  $\beta_{\text{Zr}} + \alpha_{\text{Zr}} + \alpha_{\text{Ce}}$  is outlined where  $\beta_{\text{Zr}}$  composition corresponds to (89 at.% zirconium + 0.5 at.% cerium),  $\alpha_{\text{Zr}}$  corresponds to (98.5 at.% zirconium + 0.5 at.% cerium) and  $\alpha_{\text{Ce}}$  by its composition approaches an unalloyed cerium. The three-phase  $\beta_{\text{Zr}} + \alpha_{\text{Zr}} + \alpha_{\text{Ce}}$  region is limited by three two-phase regions  $\alpha_{\text{Th-Zr-Ce}} + \beta_{\text{Zr}}$ ,  $\alpha_{\text{Zr}} + \beta_{\text{Zr}}$  and  $\alpha_{\text{Zr}} + \alpha_{\text{Ce}}$ . The presence of alloys in the three-phase state is well proved by the microstructure data. But roentgenograms of these alloys show either two lattices, one of which belonging to the  $\alpha_{\text{Th-Zr-Ce}}$  solid solution and the other to the  $\alpha_{\text{Zr}}$  or one lattice  $\alpha_{\text{Zr}}$ . The high thorium alloys of two phase region  $\alpha_{\text{Th-Zr-Ce}} + \beta_{\text{Zr}}$  have the lattice of solid solution  $\alpha_{\text{Th-Zr-Ce}}$ ; roentgenograms of the alloys of this region with a more than 70 at.% zirconium show a simultaneous presence of two lattices one of which belongs to solid solution  $\alpha_{\text{Th-Zr-Ce}}$ , and the other to  $\alpha_{\text{Zr}}$  (due to  $\beta \rightarrow \alpha$  transformation during quenching).

At 600°C there exists a region of solid solution  $\alpha_{\text{Th-Zr-Ce}}$  which is separated from a very small region of solid solution  $\alpha_{\text{Zr}}$  by a wide two-phase region of  $\alpha_{\text{Th-Zr-Ce}} + \alpha_{\text{Zr}}$  (Fig. 3d). The boundary of mutual solubility of zirconium and cerium in thorium at 600°C passes from 7 at. % zirconium in the thorium-zirconium binary system to 5 at. % (Zr + Ce) in the section cutting the thorium corner of the system at a ratio of Zr : Ce = 1 : 1 and then goes in close vicinity of the thorium-cerium binary system; solid solution  $\alpha_{\text{Th-Zr-Ce}}$  in the section cutting the zirconium corner of the system at a ratio of Th : Ce = 1 : 1 contains about 1 at. % zirconium. The alloys quenched from 600°C have two crystal lattices: face-centred cubic of solid solution  $\alpha_{\text{Th-Zr-Ce}}$  and hexagonal lattice of  $\alpha_{\text{Zr}}$ . These two lattices are observed simultaneously only in the alloy with 60 at.% (Th + Ce) in the section cutting the zirconium corner of the system at a ratio of Th : Ce = 1 : 1. But the roentgenographs of the rest alloys studied show the lattice of that phase whose quantity prevails in a given alloy.

### 3. THE THORIUM-ZIRCONIUM-NIOBIUM SYSTEM

In some of the studied ternary systems containing thorium, in examining a crystal structure of alloys of  $\beta_{\text{Zr}}$  solid solution found regions of alloys were found in which upon quenching there appeared a hexagonal lattice of the metastable  $\omega$  phase (1) (2). The formation of  $\omega$  phase in alloys is accompanied by a considerable increase of their hardness.

In the thorium-zirconium-niobium system the influence of the cooling rate on formation of the  $\omega$  phase in quenching the alloys from the region of  $\beta_{\text{Zr}}$  solid solution was studied and the kinetics of metastable  $\beta$  phase decomposition in tempering was observed. Experiments were held on three series of specimens: quenched at 1000°C after holding them at this temperature during 48 hours in icy water with breaking a quartz ampule; quenched at 1000°C in icy water without breaking a quartz ampule and quenched at 1300°C after holding them at this temperature during three hours in icy water with breaking a quartz ampule.

On the basis of data of x-ray analysis and hardness of the alloys, quenched at 1000°C in icy water with breaking a quartz ampule in fig. 4a the distribution of metastable phases in the tho-

rium-zirconium-niobium system in the region of ternary  $\beta_{Zr}$  - base solid solution is shown. In alloys containing 98, 96 and 95 at. % zirconium, located in the section, cutting the zirconium corner of the system at a ratio of  $Th : Nb = 1 : 1$   $\beta \rightarrow \alpha'$  martensite transformation takes place upon quenching. The same transformation is observed in alloys with 2 and 4 at. % niobium located in the section with the constant zirconium content of 90 at.%. The increase of niobium content up to 5 at.% in the alloys of this section brings to the formation of a certain amount of  $\omega$  phase in connection with development of the  $\beta \rightarrow \omega$  transformation. The amount of  $\omega$  phase increases in alloys of this section with further increase of niobium content in them. In these alloys as well as in the zirconium binary alloy containing 10 at.% niobium  $\beta$  and  $\omega$  phase lattices are observed. In alloys containing 1 and 3 at.% niobium, located in the section of a constant zirconium content of 85 at.% during quenching  $\beta \rightarrow$  transformation occurs. At 5 at.% niobium content partial stabilization of  $\beta$  phase takes place. In the rest of the studied alloys located in the sections of constant zirconium contents of 80, 75 and 70 at.%  $\beta$  phase is stabilized.

In accordance with the metastable phases observed after quenching the hardness of the alloys is changed as well. In the alloys where  $\beta \rightarrow \alpha'$  transformation takes place the hardness somewhat increases. With development of  $\beta \rightarrow \omega$  transformation and increase of the quantity of the  $\omega$  phase a sharp increase of hardness is observed which for ternary alloys sums up  $\sim 320 \text{ kg/mm}^2$ . The stabilization of  $\beta$  phase results in a decrease of the hardness. The increase of the hardness of the alloys, located in the sections with 80 and 75 at.% zirconium, at increasing niobium content where during quenching  $\beta$  phase is observed is caused by alloying of  $\beta$  - solid solution. In the binary alloys of zirconium containing 3 to 5 at. % niobium the hardness increases in conjunction with the occurrence of the  $\beta \rightarrow \alpha'$  transformation in them. A further increase of the hardness up to  $\sim 310 \text{ kg/mm}^2$  for alloys containing up to 10 at.% niobium is caused by the formation of  $\omega$ -phase. Partial stabilization of  $\beta$  phase lowers the hardness of alloys containing up to 15 at.% niobium up to  $190 \text{ kg/mm}^2$ .

Thus in alloys quenched at  $1000^\circ\text{C}$  in icy water with breaking a quarte ampule  $\omega$ -phase appearing in the zirconium-niobium binary system at a concentration interval of 5 to 15.5 at.% niobium is spreading to the ternary thorium-zirconium-niobium system in the section with 90 at.% zirconium up to 5.5 at.% thorium, and in the section of 85 at.% zirconium - up to 9 at.% thorium. In the remaining alloys of these sections as well as high zirconium alloys an alpha phase is observed. In alloys located in the sections of 80, 75 and 70 at.% zirconium the  $\beta$  phase is stabilized.

As illustrated in Fig.4b on icy water quenching at  $1300^\circ\text{C}$  with breaking the ampule a somewhat different picture of distribution of metastable phases in the thorium - zirconium - niobium system is observed.

Already in the alloys containing 96 and 95 at.% zirconium in the section cutting the zirconium corner of the system at a ratio of  $Th : Nb = 1 : 1$  the  $\beta \rightarrow \alpha'$  transformation is partially suppressed by the  $\beta \rightarrow \omega$  transformation. In the alloy with 2 at.% niobium with constant zirconium content of 90 at.% in the section also a partial suppression of the  $\beta \rightarrow \alpha'$  transformation is observed. An increase of niobium content in the alloys of this section brings to the development of  $\beta \rightarrow \omega$  transformation, as a result of which already in the alloy of 5 at.% niobium content  $\beta$  and  $\omega$



phase lattices are observed. In an alloy with 3 at.% niobium in the section with 85 at.% zirconium alongside  $\beta \rightarrow \alpha$  transformation there occurs a partial stabilization of the  $\beta$  phase; in alloys with 7 and 8.5 at.% niobium  $\beta \rightarrow \alpha'$  transformation is completely suppressed by  $\beta \rightarrow \omega$  transformation, and in an alloy with 10 at.% niobium  $\beta$ ,  $\omega$  and  $\alpha'$  phases are again observed. But in the binary alloy of zirconium with 15 at.% niobium  $\beta$  phase lattice becomes stabilized. It is worthy of note that in the zirconium-niobium binary alloys  $\omega$  phase spreading region is also widening;  $\omega$  phase is already observed in an alloy with 3 at.% niobium.

Thus on quenching at 1300°C as compared with hardening at 1000°C in icy water with breaking a quartz ampule an extension of  $\omega$  phase formation region is observed to the side of higher zirconium content both in the alloys of the zirconium-niobium binary system and in the alloys of the thorium-zirconium-niobium ternary system. For example in the zirconium-niobium binary alloys in quenching at 1300°C  $\omega$  phase spreading region begins already at 2.5 at.% niobium instead of 5 at.% niobium as is the case in hardening at 1000°C. In ternary alloys located in the section which cuts the zirconium corner of the system at a ratio of Th : Nb = 1 : 1 the  $\beta \rightarrow \omega$  transformation in quenching at 1300°C begins already at 96 at.% zirconium in the alloy while at quenching at 1000°C in these alloys only  $\beta \rightarrow \alpha'$  transformation takes place. In alloys located in sections of constant zirconium contents of 90 and 85 at.%  $\omega$  - phase at quenching at 1300°C is formed in alloys with 2.5 and 4 at.% niobium respectively instead of 4.5 and 6 at.% niobium as at quenching at 1000°C. In all these alloys in quenching at 1300°C the formation of  $\omega$  phase takes place owing to a partial suppression of  $\beta \rightarrow \alpha'$  transformation and the development of  $\beta \rightarrow \omega$  transformation. One may suppose that the widening of the region of  $\omega$ -phase formation in quenching at 1300°C results from the increase of thermoelastic stresses favouring the development of martensite transformation  $\beta \rightarrow \omega$  associated with the transformation of the cubic lattice of  $\beta$  phase to the hexagonal lattice of  $\omega$  phase.

Fig. 4 shows the distribution of metastable phases in thorium-zirconium-niobium alloys quenched at 1000°C in icy water without breaking a quartz ampule. Unlike the data, obtained upon icy water quenching at 1000°C with breaking a quartz ampule in alloys with 96-98 at.% zirconium in the section cutting the zirconium corner of the system at a ratio of Th : Nb = 1 : 1 not only  $\alpha'$  - phase lattice is observed but also some lines of  $\beta$  - phase lattice are observed. Also the same case is observed in the alloys with 2 and 4 at.% niobium in the section of 90 at.% zirconium as well as in the alloys with 1 and 3 at.% niobium in the section of 85 at.% zirconium in which alongside with  $\beta \rightarrow \alpha'$  transformation the  $\beta$  phase is partially stabilized.

In the alloys with 2 and 5 at.% niobium in the section of 80 at.% zirconium and in those with 5 at.% niobium in the section of 75 at.% zirconium in which in icy water quenching at 1000°C with breaking a quartz ampule  $\beta$  phase becomes stabilized at a lower cooling rate (quenching without breaking a quartz ampule) a partial  $\beta \rightarrow \alpha'$  transformation takes place as a result of which the alloys mentioned contain  $\alpha'$  and  $\beta$  phases. In the alloys with 6 and 7 at.% niobium by the section of 90 at.% zirconium  $\omega$  phase is formed but unlike the alloys quenched at 1000°C with breaking a quartz ampule in which  $\omega$  and  $\beta$  phases are observed in this case  $\alpha'$  phase is observed as well as a result of the  $\beta \rightarrow \alpha'$  transformation occurring partially. Similar case is observed in the alloys with 5 and 7 at.% niobium by the section of 85 at.% zirconium.



Thus at decreasing the cooling rate in icy water quenching at 1000°C with breaking a quartz ampule in the region of high zirconium alloys approaching the thorium-zirconium binary system by their composition where at a higher cooling rate  $\alpha'$  phase was observed, besides  $\alpha'$  phase  $\beta$  phase is observed. It is possible to assume that this is conditioned by the presence of diffusion processes which bring to the redistribution of alloying components in microvolumes of the alloys with concentrations of stable  $\beta$  - phase.  $\omega$  phase being formed in the zirconium-niobium binary system at the interval of from 5 to 13 at.% niobium concentration spreads over the thorium-zirconium-niobium ternary system by the section of 90 at.% zirconium up to 4.5 at.% thorium and by the section of 85 at.% zirconium and from 5 to 12 at.% thorium which does not indicate to the considerable change of its spreading region as compared with this region at 1000°C quenching in icy water with breaking a quartz ampule.

It is known that  $\omega$  - phase can arise both in a non-diffusive way at quenching and straining and at tempering metastable  $\beta$  phase where  $\omega$ -phase formation is associated with the diffusion process. With the aim of finding out transformation processes from the metastable  $\beta$  phase to the mixture of stable phases in the thorium-zirconium-niobium system the tempering of alloys was investigated at temperatures of 100°, 200°, 300°, 400° and 500°C by holding them during 0.25, 0.5, 1, 5, 10, 50 and 100 hours at each of these temperatures. Before tempering the alloys were quenched at 1000°C in icy water with breaking a quartz ampule from the stability region of  $\beta$  phase. Decomposition process was controlled by X-ray analysis and hardness determination. For studying the decomposition of  $\beta$  - phase one zirconium binary alloy with 20 at.% niobium, three alloys with the section of constant 80 at.% zirconium content with 5, 10 and 15 at.% niobium as well as two alloys with the section of constant 10 at.% niobium content with 70 and 75 at.% zirconium were chosen. All these alloys are quenched at the stabilization of  $\beta$  - phase.

Out of the alloys tempered at 100°C only in the alloy with (80 at.% zirconium + 5 at.% niobium) after holding it during 50 hours  $\omega$  phase formation is observed the amount of which increases after 100 hours holding together with the increase of its hardness up to 120 kg/mm<sup>2</sup>. The rest of the alloys at this tempering temperature retain the  $\beta$  - phase lattice and practically do not change their hardness as compared with the hardness in a quenched state.

In tempering at 200°C in all alloys except the binary alloy of zirconium with 20 at.% niobium  $\beta$  - phase decomposes with the formation of  $\omega$  phase. In alloys located in the section of 80 at.% zirconium  $\beta$  - phase stability increases with the increase of niobium content. For example in a 5 at.% niobium alloy the  $\beta \rightarrow \omega$  transformation begins already after 0.25 hour tempering ; in a 10 at.% niobium alloy it begins after 5 hours tempering and in a 15 at.% niobium alloy it begins after 10 hours tempering. While in a binary alloy of this section of 20 at.% niobium  $\beta$  phase at this tempering temperature remains stable during the whole period of testing (100 hours). The formation of  $\omega$  phase is fixed both in roentgenograms of the studied ternary alloys by the occurrence of  $\omega$  phase lattice lines and by the increase of hardness of the alloys. In the alloy with (75 at. % zirconium + 10 at.% niobium) the  $\beta \rightarrow \omega$  transformation is observed already after 50 hours holding. The increase of the holding time to 100 hours brings to the increase of  $\omega$  phase region formed which is confirmed by a further growth of the alloy hardness. In the alloy with

(70 at.% zirconium + 10 at.% niobium) in tempering at 200°C after five hours holding the  $\beta$  - phase decomposition takes place not only with  $\omega$  - phase formation, but also with the formation of equilibrium  $\alpha_{Th}$  phase at low temperatures. In the roentgenogram of this alloy lines of  $\beta$ ,  $\omega$  and  $\alpha_{Th}$  phases are observed. With the increase of tempering time the alloy hardness at first sharply increases and then this increase becomes lower which is associated with the beginning of  $\alpha_{Th}$  - phase coagulation process.

In tempering at 300°C in all alloys except the binary alloy of zirconium with 20 at.% niobium  $\beta$  - phase decomposition takes place alongside with the formation of both  $\omega$  - phase and  $\alpha_{Th}$  phase. In the section of 80 at.% zirconium the  $\beta \rightarrow \omega$  transformation is observed after 0.25 - hour tempering in a 5 at.% niobium alloy, in the alloys with 10 and 15 at.% niobium it is observed after 1 hour tempering and in a binary alloy with 20 at.% niobium it is observed after 50 hours tempering. In tempering at 300°C. in the same alloys  $\alpha_{Th}$  phase occurs too whose precipitation sharply increases the hardness as a result of a dispersion hardening. With the increase of tempering time as a result of the coagulation process of fine-dispersion precipitations of  $\alpha_{Th}$  phase a certain softening of alloys occurs. In the alloys with (75 at.% zirconium + 10 at.% niobium) and (70 at.% zirconium + 10 at.% niobium) the  $\alpha_{Th}$  phase precipitation takes place simultaneously with the  $\beta \rightarrow \omega$  transformation. In tempering alloys at 400°C as at 300°C  $\beta$  - phase decomposition in the studied alloys takes place through  $\omega$  - phase formation as a result of the  $\beta \rightarrow \omega$  transformation. At the same time the process of  $\alpha_{Th}$  - phase precipitation is taking place. In tempering at 500°C  $\beta$  - phase decomposition occurs with formation of equilibrium phases of the system. In the alloys with 5 and 10 at.% niobium located by the section of 80 at.% zirconium after 0.25 hour tempering the formation of  $\alpha_{Th}$  and  $\alpha_{Zr}$  phases is observed; in at 15 at.% niobium alloy the  $\beta$  - phase is stable during 10 hours. After holding at 500°C during 50 hours the hardness begins to grow which is connected with the precipitation of the equilibrium  $\alpha_{Th}$  and  $\alpha_{Zr}$  phases. In a binary alloy with 20 at.% niobium  $\beta$  - phase decomposition is observed after 5 hours tempering with the precipitation of  $\alpha_{Zr}$  phase. In the alloys with (75 at.% zirconium + 10 at.% niobium) and (70 at.% zirconium + 10 at.% niobium) at the beginning of the temper  $\alpha_{Th}$  - phase precipitation occurs with hardness becoming higher and then somewhat lower in connection with a partial coagulation of fine-dispersion precipitation of  $\alpha_{Th}$ . After an hour tempering another increasing of hardness takes place in connection with the precipitation of  $\alpha_{Zr}$  phase.

Thus the tempering of the studied thorium-zirconium-niobium alloys at 100-500°C during 100 hours has shown that  $\beta$  - phase decomposition at temperatures of 100-400°C as a result of the diffusion processes bringing to the formation of different alloying component concentrations in microvolumes of the alloys takes place in them through the formation of  $\omega$  phase owing to the  $\beta \rightarrow \omega$  transformation accompanied by the increase of the hardness. In those alloys where the  $\beta$  - phase decomposition in tempering at 200-400°C takes place not only with the  $\omega$  phase forming but also with the equilibrium  $\alpha_{Th}$  phase precipitation the tempering process consists of two stages: a "hardening" stage at which the hardness of alloys grows in connection with the  $\beta \rightarrow \omega$  transformation and the precipitation of  $\alpha_{Th}$  phase fine-dispersion particles and "softening" stage at which the hardness of the alloys decreases in connection with the coagulation processes

of fine-dispersion precipitations of the  $\alpha_{Th}$  phase. In tempering at 500°C during 100 hours  $\beta$  - phase decomposes with the formation the phases of the equilibrium system  $\alpha_{Th}$  and  $\alpha'_{Zr}$ .

#### 4. THE THORIUM-ZIRCONIUM-MOLYBDENUM SYSTEM

In the thorium-zirconium-molybdenum system at 1000°C spreading limits of the region of Th-Zr-Mo ternary solid solution were found based on the body-centered cubic lattice which expands from the zirconium corner of the system by the section cutting this corner at a ratio of Th : Mo = 1 : 1 to 15.5 at.% (Th + Mo); with the increase of molybdenum content the boundary of solid solution approaches the zirconium-molybdenum binary system in which the solubility of molybdenum at 1000°C is limited to 10.5 at.%; at the increase of thorium content the boundary of the ternary solid solution approaches the thorium-zirconium binary system (fig. 5a).

In alloys of this solid solution quenched at 1000°C in icy water with breaking a quartz ampule the region of alloys was found in which as a result of a partial martensite transformation alongside with  $\beta$  - phase body-centered cubic lattice a hexagonal lattice of  $\omega$  - phase is observed (fig. 5a). In fig. 5a other metastable phases in the quenched alloys of  $\beta_{Th}$ ,  $\beta_{Zr}$ ,  $\beta_{Mo}$  solid solution are also shown.

A combined consideration of the data of x-ray analysis and hardness examination enables to arrive at a conclusion that in quenching at 1000°C in icy water with breaking a quartz ampule in the zirconium-molybdenum binary alloys alongside with a  $\beta$  phase associated with the  $\beta \rightarrow \omega$  transformation the  $\omega$  - phase is formed in the region of 1.5 to 6 at.% molybden concentrations; in tempering the alloys of lower molybden content  $\beta \rightarrow \alpha'$  transformation takes place, and in the alloys with 6 at.% molybden and more  $\beta$  phase is stabilized. In the ternary alloys of thorium with zirconium and molybdenum by the section cutting the zirconium corner of the system at a ratio of Th : Mo = 1 : 1 alongside with the  $\beta$  phase  $\omega$  - phase extends from 3.5 to 8.5 at.% (Th + Mo); for a small content of alloying additions  $\alpha'$  and  $\beta$  phases are observed; in the alloys with 9 at.% (Th + Mo) and more there occurs stabilization of  $\beta$  phase. The  $\omega$  - phase is observed also in the alloys of the sections with constant zirconium content equal to 95 at.% in the region of from 1.5 to 5 at.% molybdenum concentrations, at 93 at.% zirconium  $\omega$  phase is observed at molybdenum concentrations of from 1 to 4 at.% and in the section of 90 at.% zirconium  $\omega$  phase is observed in the alloys with 1.5 and 2 at.% molybdenum. According to the studied sections of constant zirconium content of 95, 93 and 90 at.% in the alloys containing more than 5, 4 and 2 at.% molybdenum respectively  $\beta$  phase is stabilized; in the alloys of sections of 95 and 93 at.% zirconium, containing less than 1.5 and 1 at.% molybdenum respectively owing to the  $\beta \rightarrow \alpha'$  transformation  $\alpha'$  phase is observed.

The increase of a cooling rate in quenching the alloys at 1300°C brings to the broadening of the region of the  $\omega$  - phase formation in the direction of higher content of both zirconium and thorium. As it is seen from fig. 5b where distribution of metastable phases in the Th-Zr-Mo system in quenching at 1300°C is shown in the zirconium-molybdenum binary alloys  $\omega$  - phase region is expanding to the direction of the alloys rich in zirconium up to 99 at.% zirconium.

In ternary alloys of the section cutting the zirconium corner of the system at a ratio of Th : Mo = 1 : 1 the  $\omega$  - phase field is spreading till 99 at.%

zirconium instead of 90 at.% as quenched at 1000°C. In alloys of this section of 1 and 2 at.% (Th + Mo) the increase of the cooling rate in quenching brings to the development of the  $\beta \rightarrow \omega$  transformation alongside with  $\beta \rightarrow \alpha'$  one and in alloys with 3 and 3.5 at.% (Th + Mo) the  $\beta \rightarrow \alpha'$  transformation is completely suppressed by the  $\beta \rightarrow \omega$  transformation. In the alloys located in the sections of 95 and 93 at. % zirconium expansion of the region of the  $\omega$  - phase formation is also observed in the direction of higher thorium contents due to both partial and complete suppression of the  $\beta \rightarrow \alpha'$  transformation by the  $\beta \rightarrow \omega$  transformation. In the alloys of this section, containing only 0.5 at.% molybdenum already  $\omega$  - phase is formed.

Thus the increase of a cooling rate for the zirconium-molybden and thorium-zirconium-molybden alloys quenched at 1300°C brings to the expansion of the region of the  $\omega$  - phase formation in the direction of growing content of both zirconium and thorium. One may suppose that this is conditioned by the increase of thermoelastic stresses, contributing to the development of martensite transformation of  $\beta \rightarrow \omega$ , associated with the reconstruction of the cubic lattice of  $\beta$  - phase into the hexagonal lattice of the  $\omega$  - phase.

The decrease of a cooling rate during a slow quenching of the alloys at 1000°C without breaking a quartz ampule also brings to the expansion of the region of the  $\omega$  - phase formation to the direction of alloys more rich in zirconium both in the zirconium - molybdenum binary alloys and in the zirconium-thorium-molybden ternary alloys located in the section which cuts the zirconium corner of a system at a ratio of Th : Mo = 1 : 1 (fig. 5c). In all studied alloys located in sections of a constant zirconium content of 95 and 93 at.%  $\omega$  - phase formation is observed. Addition to the zirconium-thorium binary alloys in which at this quenching rate  $\alpha'$  phase is observed of only 0.5 at.% molybdenum brings to the formation of  $\beta$  and  $\omega$  - phases. The widening of  $\omega$  phase formation region at slow quenching seems to be connected with the presence of diffusion processes owing to which redistribution of alloying components in the microvolumes of the alloys takes place up to "critical" concentration at which the martensite transformation of  $\beta \rightarrow \omega$  occurs.

In order to elucidate decomposition process of  $\beta$  metastable phase in the thorium - zirconium - molybdenum system the temper of quenched alloys was studied at the temperatures of 100, 200, 300, 400, 500 and 600°C at holding them during 0.25; 0.5; 1; 10; 50 and 100 hours at each of these temperatures. For studying the decomposition of  $\beta$  - phase one zirconium binary alloy with 7 at.% molybdenum, four alloys with the section of constant 93 at % zirconium content with 0.5; 1; 1.5 and 2 at % thorium as well as an alloy with 92 at.% zirconium and 2 at.% thorium were chosen. All these alloys are quenched at the stabilization of  $\beta$  - phase.

In tempering at 100°C during 100 hours in all alloys studied metastable  $\beta$  - phase is preserved. In this case the hardness of the alloys practically remains constant. In tempering at 200°C  $\beta$  - phase is preserved only in a binary alloy with 7 at.% molybdenum; addition of only 0.5 and 1 at % thorium to this alloy brings to the decomposition of  $\beta$  - phase together with the formation of  $\omega$  - phase in the course of 100 and 50 hours respectively. The increase of thorium content up to 1.5 at % in the alloys of a section with 93 at % zirconium results in  $\beta$  phase decomposition already after 5 hours tempering. For the same period of time  $\beta$  phase decomposition is observed in the alloy with 95 at % zirconium and 2 at % thorium as well. In tempering at

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300°C in all ternary alloys studied  $\beta$  phase decomposition together with  $\omega$  - phase formation is observed already after first 0.25 hour tempering; in the binary alloy with 7 at % molybdenum this decomposition begins after 1 hour tempering. The hardness of all alloys studied after 100 hours tempering reaches  $\sim 440 \text{ kg/mm}^2$ .

In tempering at 400°C  $\beta$  phase decomposition together with  $\omega$  phase formation is also observed already after 0.25 hour tempering. But the growth of the hardness at this temperature takes place more rapidly and reaches  $480\text{-}500 \text{ kg/mm}^2$  in ternary alloys and  $560 \text{ kg/mm}^2$  in a binary alloy with 7 at % molybdenum. In hardening at 500°C in a binary alloy with 7 at % molybdenum during 0.5 hour  $\omega$  phase formation is observed and during 1 hour and more in this alloy  $\alpha\text{Zr}$  equilibrium phase is formed. The hardness of this alloy increases in connection with  $\omega$  phase and  $\alpha\text{Zr}$  phase formation. In all ternary alloys studied a comparatively small growth of the hardness during first hours of tempering (up to  $\sim 380 \text{ kg/mm}^2$ ) is caused by the formation of  $\omega$  phase and occurrence of  $\alpha\text{Zr}$  phase; lowering of the hardness is caused by coagulation of fine-dispersion precipitation of  $\alpha\text{Zr}$  phase. In hardening at 600°C in all alloys studied at the formation of  $\alpha\text{Zr}$  equilibrium phase  $\beta$  phase decomposes already after 0.25 hour tempering. The growth of the hardness up to  $\sim 420 \text{ kg/mm}^2$  in zirconium binary alloy with 7 at % molybdenum and up to  $\sim 340\text{-}360 \text{ kg/mm}^2$  in ternary alloys is caused by the formation of fine-dispersion precipitation of  $\alpha\text{Zr}$ ; their coagulation brings to the lowering of the hardness.

### CONCLUSIONS

1. A projection of the equilibrium diagram of the thorium-zirconium-titanium system is constructed in the temperature range from 1000 till 500°C. Existence of a wide region of solid solutions at high temperatures is shown which are based on a body centered cubic lattice limited by a decomposition region into two solid solutions  $\beta_{\text{Th-Zr}} + \beta_{\text{Zr}}$ .

2. In the thorium-zirconium-cerium system the region of ternary solid solutions based on a body centered cubic lattice of  $\beta$  zirconium is limited by low solubility of cerium in zirconium at the temperatures studied. The region of  $\alpha_{\text{Th-Zr-Ce}}$  solid solution in the ternary system by its composition approaches the thorium-cerium binary system; at 930°C the solubility curve approaches an additive line.

3. In the thorium - zirconium - niobium and thorium - zirconium - molybdenum systems regions of alloys of  $\beta$  solid solution were found in which on quenching at different cooling rates metastable  $\omega$  phase is formed. A decomposition process of metastable  $\beta$  phase in these systems at tempering is shown.

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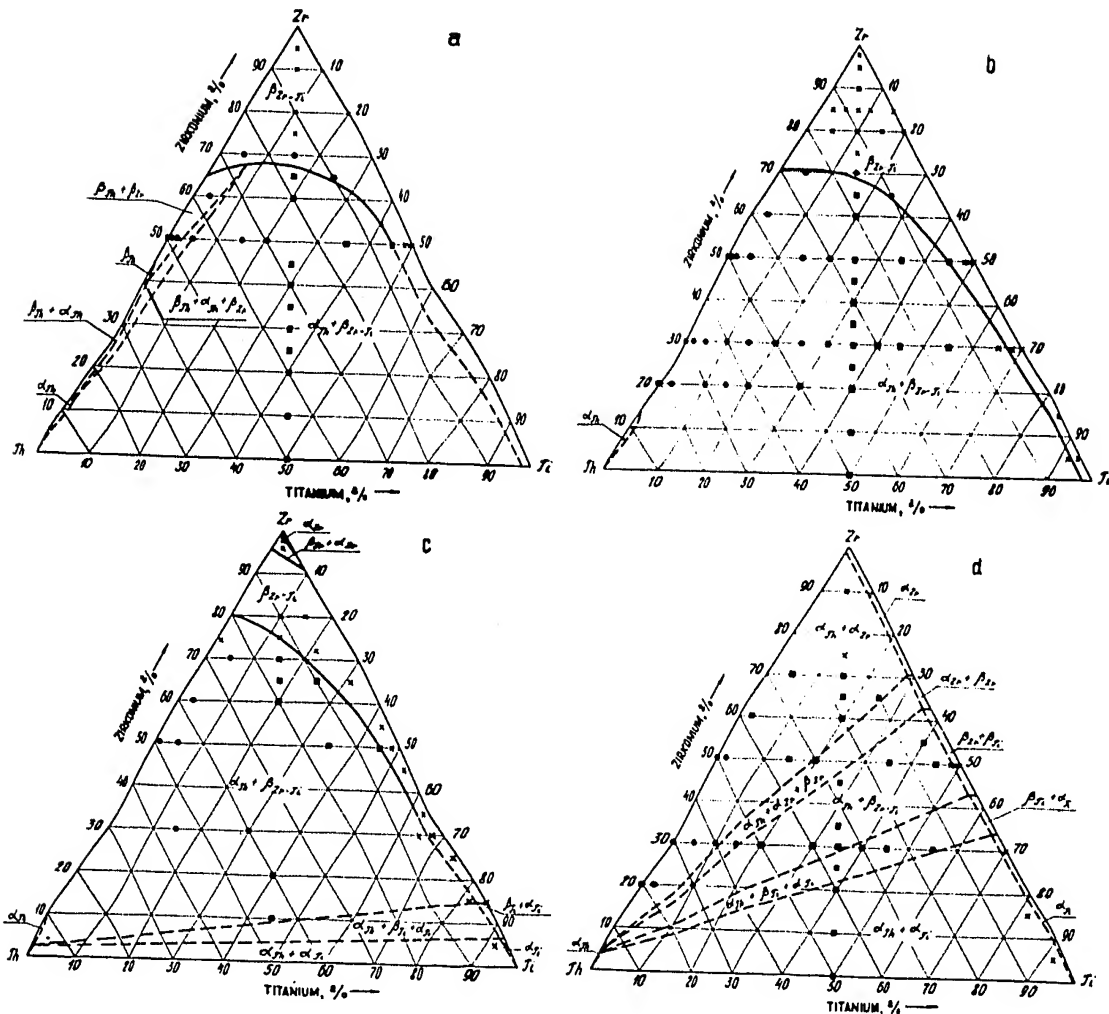


FIG.1. ISOTHERMAL SECTIONS OF EQUILIBRIUM DIAGRAM OF THE Th-Zr-Ti SYSTEM: 930°C (a); 900°C (b); 800°C (c); 600°C (d). x - hcp; ● - fcc; ■ - fcc, + hcp; ○ - bcc.

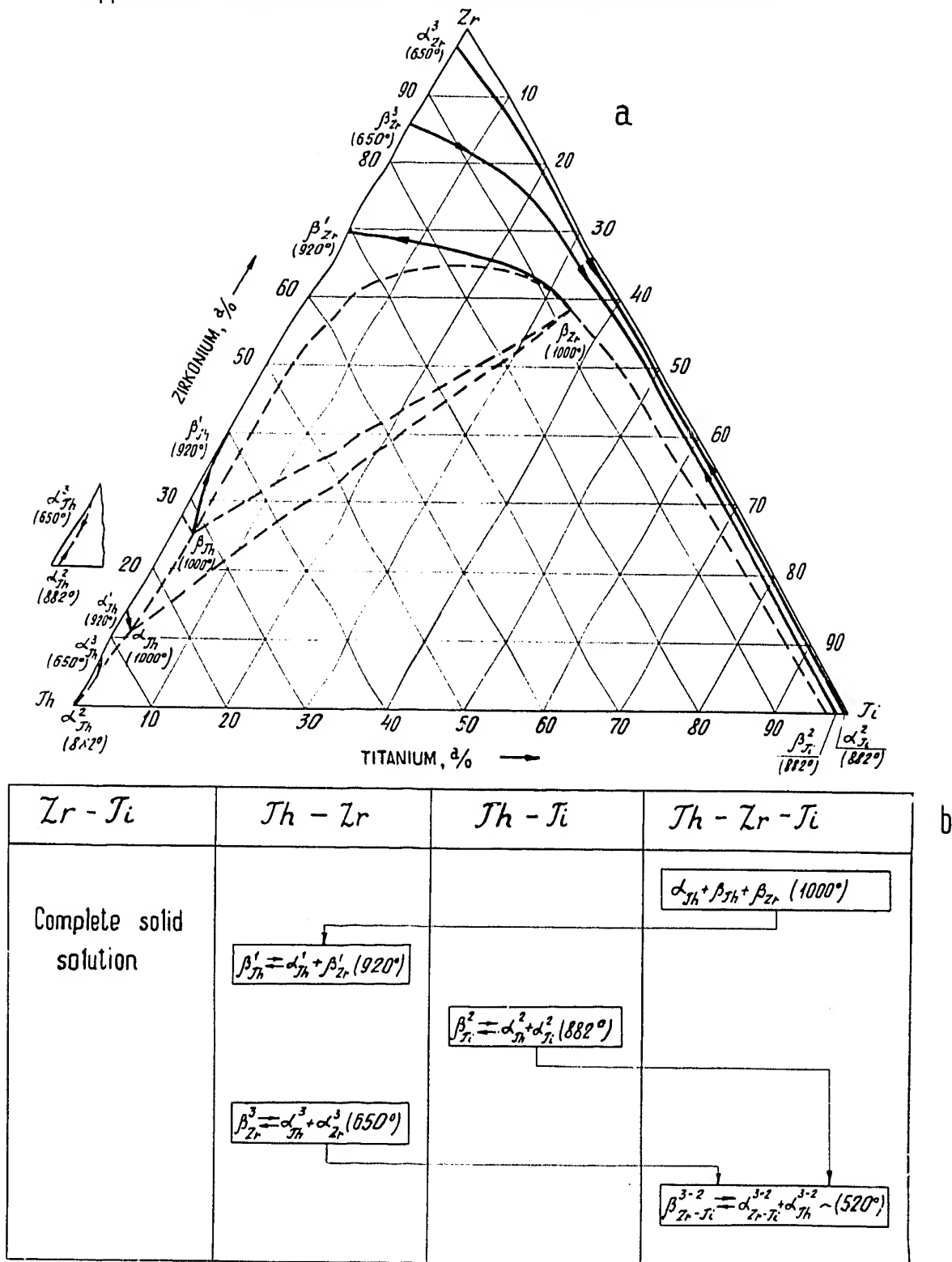


FIG.2. PROJECTION OF EQUILIBRIUM DIAGRAM OF THE THORIUM - ZIRCONIUM - TITANIUM SYSTEM

(a) and reaction scheme (b)



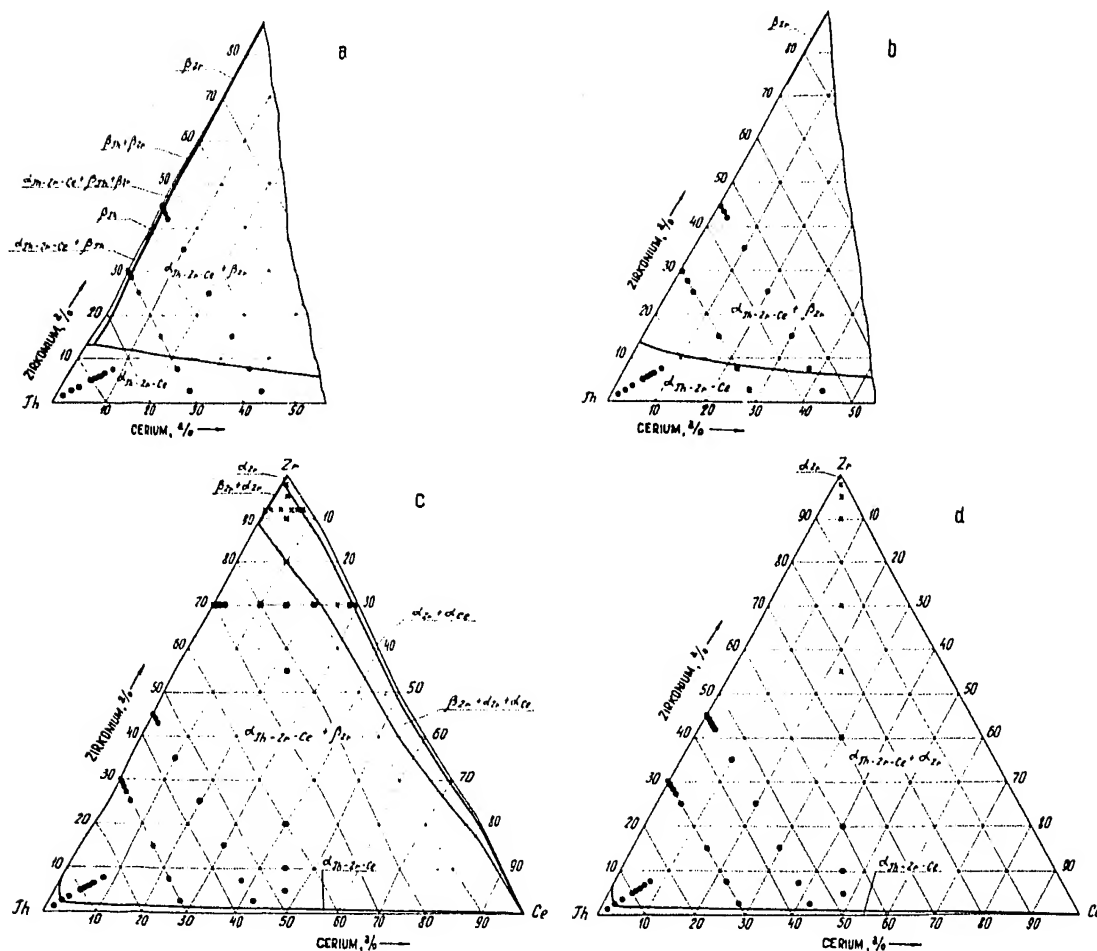


FIG.3. ISOTHERMAL SECTIONS OF THE EQUILIBRIUM DIAGRAM OF THE Th - Zr - Ce SYSTEM:  
930° (a), 900° (b), 680° (c), 600° (d).  $\times$  - hcp;  $\bullet$  - fcc,  $\blacksquare$  - fcc + hcp.

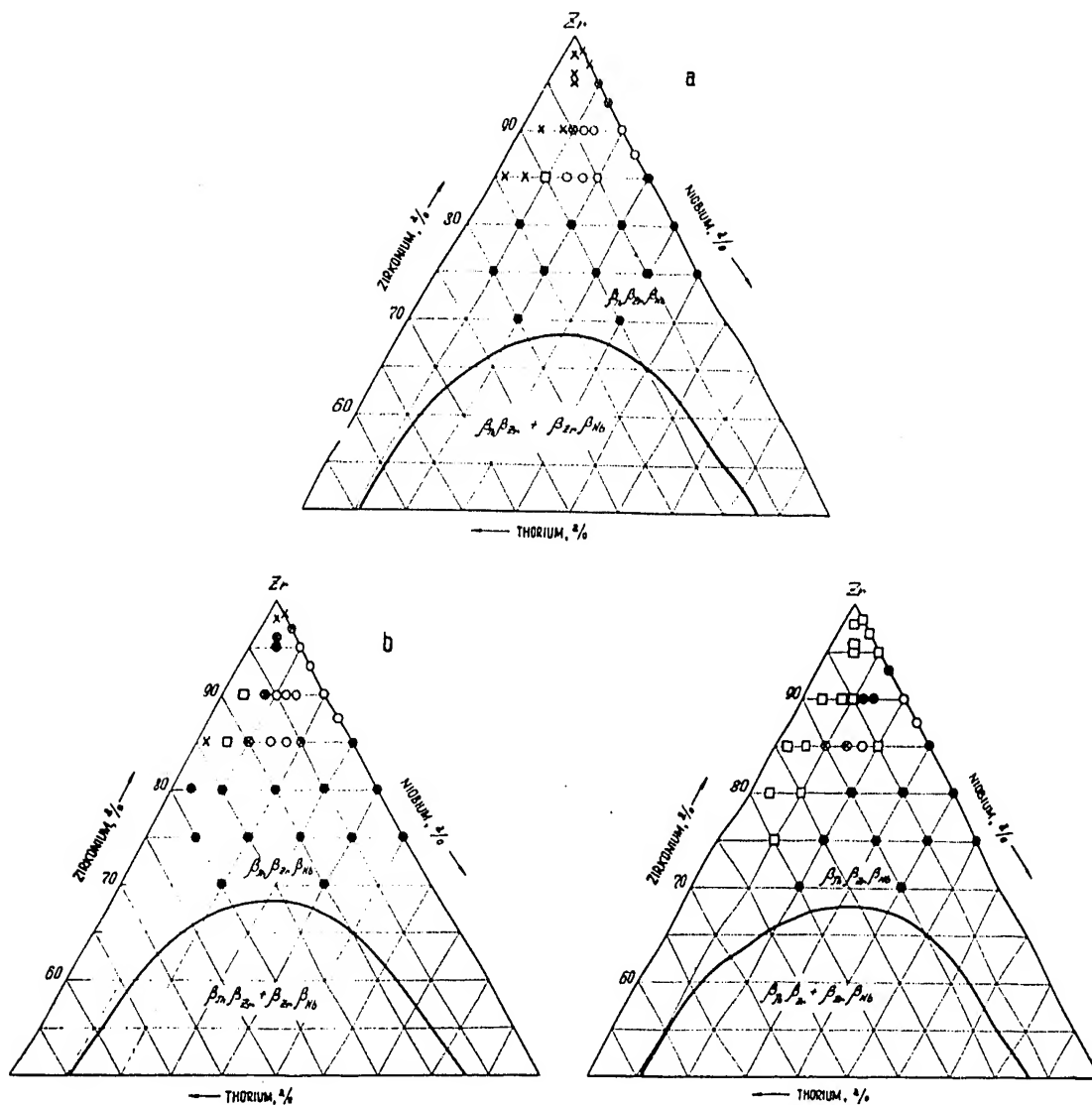


FIG.4. DISTRIBUTION OF METASTABLE PHASES IN THE Th - Zr - Nb SYSTEM AFTER  
 QUENCHING AT 1000°C IN ICY WATER  
 with breaking a quartz ampule (a), without breaking a quartz ampule (c), after quenching at  
 1300°C with breaking a quartz ampule (b). x -  $\alpha'$ ;  $\oplus$  -  $\alpha' + \beta + \omega$ ;  $\square$  -  $\alpha' + \beta$ ;  $\circ$  -  $\beta + \omega$ ;  
 $\bullet$  -  $\beta$ .

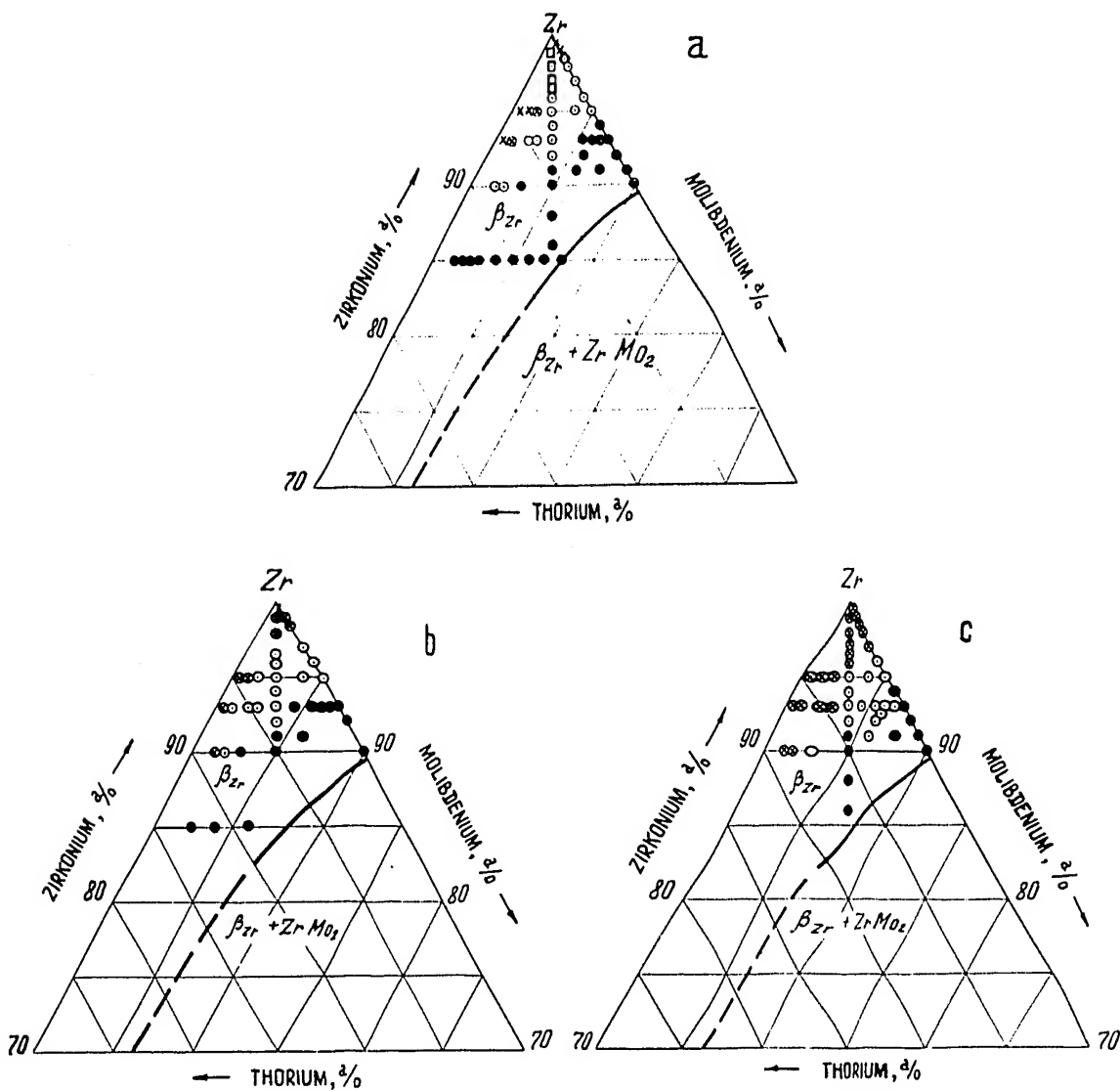


FIG.5. DISTRIBUTION OF METASTABLE PHASES IN THE Th-Zr-Mo SYSTEM AFTER QUENCHING AT 1000°C

in icy water with breaking a quartz ampule (a), in icy water without breaking a quartz ampule (c), after quenching from 1300°C with breaking a quartz ampule (b). x -  $\alpha$ ;  
 $\oplus$  -  $\alpha + \beta + \omega$ ;  $\square$  -  $\alpha' + \beta$ ;  $\circ$  -  $\beta + \omega$ ;  $\bullet$  -  $\beta$ .